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Organometallic Compounds and Polymers with Second and Third order Nonlinear Optical Properties

covering 12/1/89 through 11/30/92

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Summary

The chemistry carried out with AFOSR support was aimed at exploring new materials with potentially interesting nonlinear optical properties. All of our work involved transition metal complexes. In these materials we can alter either the metal ion or the ligands independently. In this way it is possible to alter the electronic properties of a given complex without altering its molecular or solid-state structure. Second and third order NLO properties were investigated in these materials. Both molecular and bulk nonlinearities were examined as second order candidates, while only molecular nonlinearities were examined for the third order materials.

Manganese complexes were prepared which crystallize into infinite polar polymeric chains. The polar order along these chains is excellent, and is unaffected by significant alteration of the organic ligands. Unfortunately, these polar chains pack with an antiparallel orientation in the solid-state. The crystal structures of several of these complexes were reported.

A number of monomeric complexes are also described. One of the monomeric coordination compounds $[(\text{SALEN})\text{Fe}(\text{py})\text{N}_3]$ crystallizes in an acentric space group ($P6_5$). Kurtz powder tests performed on this material and related halide complexes show these complexes have SHG efficiencies 0.5-2 times that of the urea reference (1907 nm fundamental). Solution measurements indicate that the nonlinearity is due to the metal pyridyl system. In order to probe the utility of high valent metal pyridyl complexes for second order NLO, a number of metal picolylmethylketone complexes were prepared and examined in poled polymer films. In these complexes trivalent metal ions act as electron acceptors toward pyridyl donors. β values for identically substituted complexes fall in the order $\text{Sc} \approx \text{Cr} > \text{Fe} > \text{Co}$. We are currently investigating other metal complexes.

The third order NLO properties of organometallic complexes have also been investigated. Group IV metallocene halides, acetylides and vinyl complexes have been examined by third harmonic generation (1907 nm fundamental). All of the dihalides showed γ s lower than our

detection limit in CHCl_3 ($<5 \times 10^{-36}$ esu). Metallocene acetylides $[\text{Cp}_2\text{M}(\text{C}\equiv\text{CR})_2]$, $\text{M} = \text{Ti, Zr, Hf}$; $\text{R} = \text{Ph, } n\text{Bu}$] gave γ values between 5×10^{-36} and 90×10^{-36} esu. A detailed molecular orbital analysis suggests that the nonlinearity in these materials is due to a molecular state involving the acetylide π and metal orbitals, as well as the Cp π orbitals. Consistent with this picture is the high γ value (150×10^{-36} esu) for a dimetallic complex, *i.e.* $\text{Cp}_2\text{Zr}(\text{Cl})\text{-CH=CHC}_6\text{H}_4\text{CH=CH-Zr}(\text{Cl})\text{Cp}_2$. A number of other organometallic complexes were examined and we are currently looking at other metal complexes to learn what factors are important in optimizing γ .

Composite organic/inorganic compounds are also of interest. Layered materials have been prepared with alternating polyacetylenic and inorganic $[\text{Sn}(\text{PO}_4)_2]$ layers. Thin films of these materials (*ca* $0.5 \mu\text{M}$) supported on glass are transparent and red. The wave guiding properties and third harmonic generation efficiencies of these materials were examined and found to be poor.

Coordination polymers for 2nd order NLO

One of the goals of our work is to prepare inorganic complexes with strong polar directing character, which should lead to materials with interesting NLO properties. A number of square pyramidal coordination complexes of the type shown in Figure 1 have been prepared, which form infinite chains in the solid state. The metal atoms in these materials act as electron acceptors and the amino groups as donors, forming an electronic dipole between the metal atom of one molecule and amino group of an adjacent molecule. The nature of this coordination polymerization guarantees that the chains will have their individual dipoles aligned in a head to tail fashion. By changing the metal atom in these materials it should be possible to alter the electronic properties without significantly altering the solid-state structure, which will allow us to finely tailor the electronic properties of this class of materials. This chemistry is discussed in references 1-3 and 10.

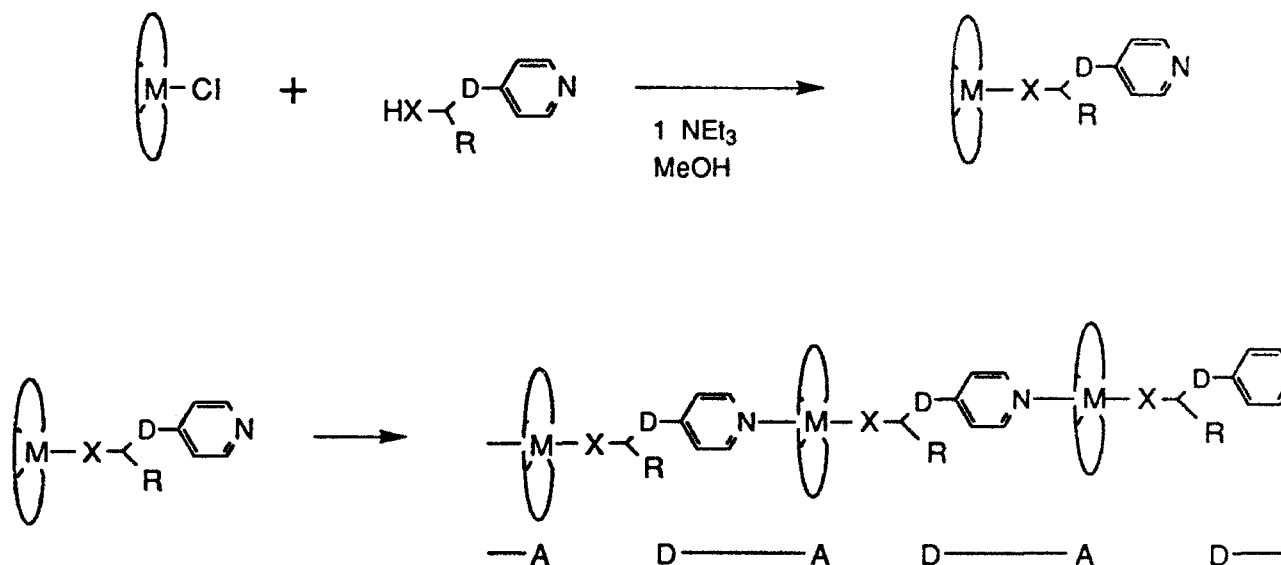


Figure 1: Synthesis of monomers (top) and dipolar coordination polymers (bottom). Ellipse = SALEN = *N,N'*-ethylenebis(salicylaldiminato)dianion; sol = solvent molecule; $M = Cr, Mn, Fe$; $X = O_2C, O_3S$.

We have prepared the compounds described in the legend of Figure 1, and structurally characterized several Mn compounds. The structually characterized materials have $X = SO_3$, $D = NH$, $R = H$; $X = SO_3$, $D = NH$, $R = isopropyl$; $X = CO_2$, $D = NH$, $R = H$; $X = CO_2$, $D = S$; $R = H$. The structures of the monomer units of several of these compounds are shown in Figure 2. All of the

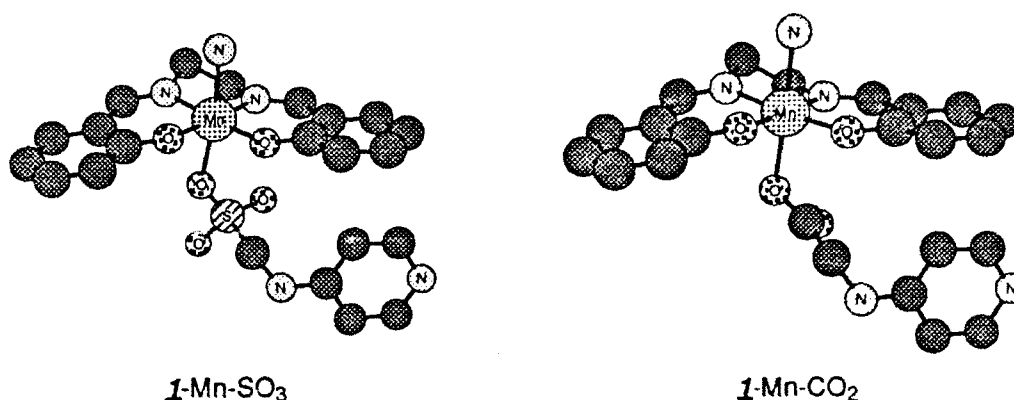


Figure 2: The molecular structures of $X = \text{SO}_3$, $D = \text{NH}$, $R = \text{H}$ and $X = \text{CO}_2$, $D = \text{NH}$, $R = \text{H}$. The pyridyl nitrogen of an adjacent molecule is shown.

monomer units have the expected coordination geometry, and form infinite polar chains in the solid state, as shown in figure 3 for one of them. The structures of all of these complexes are basically the same, as expected. Adjacent dipoles along the polymer chain are arranged with *ca* a 90° angle between their axes. Unfortunately, the polar chains pack with an antiparallel arrangement (space group = $P2_1/c$) leading to no observed 2nd order NLO properties. The Mn-N(pyridyl) bond lengths fall in the middle of the range observed for Mn^{III} -N(pyridine) bond lengths in neutral complexes. Replacement of the pyridyl group with a benzonitrile, gives a crystalline material, but not the expected coordination polymer.

Synthesis and study of new inorganic chromophores for 2nd order NLO

The goals of the previous section were to examine coordination polymerization as a means of producing polar materials and to investigate the role of transition metal ions in second order NLO. Another approach to the latter of these goals is the testing of a number of soluble complexes in solution or in polymer matrices. In this way the solid-state structural component in the NLO properties can be eliminated. In poled polymers these inorganic chromophores may have an advantage over the organic ones, in that the thermal stabilities of these inorganic chromophores are typically much greater than for organic compounds.

In our studies of metal coordination complexes, we have found a number of iron compounds which crystallize in noncentrosymmetric space groups, and give powder SHG

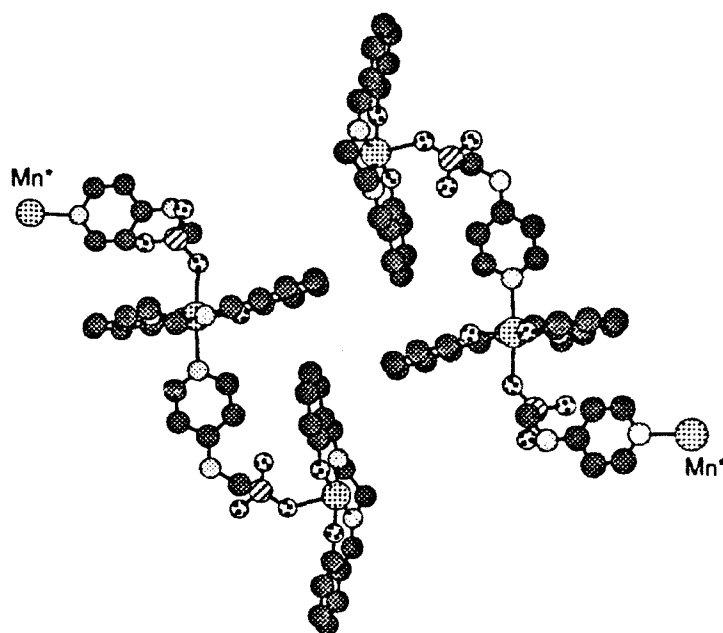
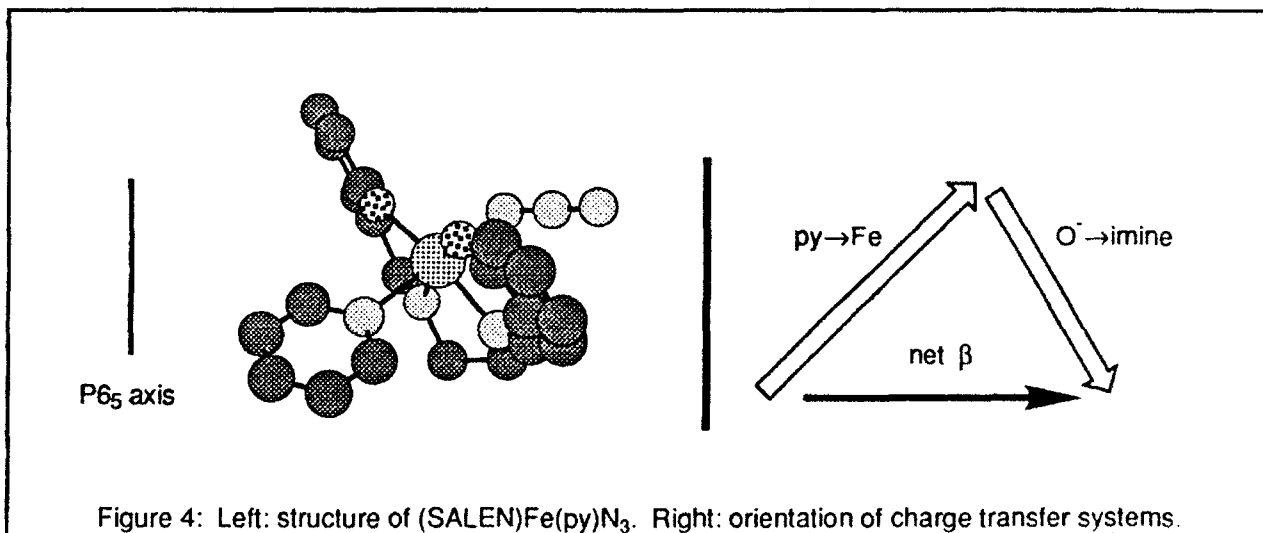
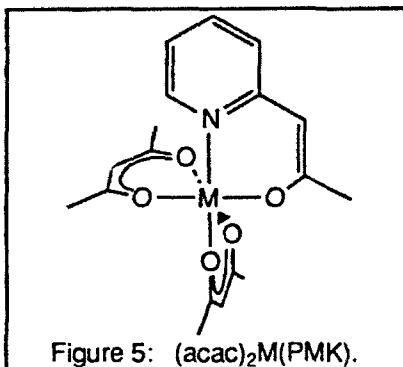


Figure 3: Packing of $X = \text{SO}_3$, $D = \text{NH}$, $R = \text{H}$ chains in the unit cell. Mn atoms in adjacent cells also shown, labeled Mn^* .

efficiencies between 0.5 and 2 times that of a urea reference $[(\text{SALEN})\text{Fe}(\text{py})\text{X}]$; $X = \text{halide}$, pseudo halide; $\text{SALEN} = N,N'$ -bisethylene(salicylimine)]. This chemistry is discussed in reference 11. The azide adduct has been crystallographically characterized, figure 4, and crystallizes in the space group $P6_5$. A likely origin for the optical nonlinearity of this complex is the pyridyl to iron charge transfer, whose axis lies at a 55° angle to the screw axis. Pyridine to metal charge transfers typically have large oscillator strengths and changes in dipole moment, both of which are necessary for a complex to have a large first hyperpolarizability. Unfortunately, the SALEN ligand also has a charge transfer system which can lead to a measurable optical nonlinearity. This system involves an alkoxide donor and an imine acceptor. The charge transfer axis of this all organic system is orthogonal to the pyridine-metal system, making an angle of -45° to the screw axis. Thus the two NLO chromophores will act to cancel each other out in this structure.

We have examined two types of molecular compounds to date in poled polymer thin films; one is aimed at looking at the organic portion of these complexes and the other at the pyridine-metal system. A thin film containing (SALEN)FeN₃ was prepared and poled. The measured electrooptic coefficients for this film at low poling fields is very similar to that observed for dimethylaminonitrostilbene (DANS) in PMMA. As the poling field is increased, however, the electrooptic coefficient decreases by *ca* 50% relative to the low field value. Two different samples showed identical decreases in activity. The likely reason for the decrease is that the NLO chromophore is decomposing during the experiment. While the data suggest that the decomposition is field dependent, both samples went through the same annealing process and poling sequence (0.3, 0.6 and 0.9 MV/cm in that order). We are currently looking at the chemistry of (SALEN)FeN₃ in high boiling esters to determine if the complex thermally converts to a characterizable species. Recently Dr. Lap Tak Cheng at du Pont (C, R & D; Willmington, Del.) examined (SALEN)FeN₃ in CHCl₃ solution by EFISH. The solubility of the complex was too low to get a reliable $\mu\cdot\beta$ value, but it is clearly not comparable to DANS. An interesting question then is what is the chromophore in PMMA that is giving rise to the observed electrooptic signal? Work is underway to answer this question, however one thing is clear, greater care needs to be taken in designing molecules that are stable in the polymer matrices.





A second type of molecule that we have investigated in poled polymer thin films is designed to examine the nonlinear optical properties the pyridine-metal charge transfer system. This chemistry is discussed in reference 8. To increase the stability of these complexes, the pyridyl groups have been incorporated into a chelated ligand, $(acac)_2M(PMK)$, $M = Sc, Cr, Mn, Fe, Co$, see figure 5. We have also recently prepared a PMK complex with OMe donor groups in the 4 position of the pyridyl ring, $(acac)_2Co(PMK-OMe)$. These complexes have been incorporated into host/guest PMMA polymer films, and poled. These measurements were carried in a transparent region for all of the samples (830 nm). Unlike the iron SALEN compound, $(acac)_2M(PMK)$ compounds do not decompose in the polymer matrix during poling. Most of the β values for these molecules are relatively low $[(3-12) \times 10^{-30} \text{ esu}]$. The one thing that is strongly suggested by this data is that the Sc, Cr and Fe compounds have larger β values than the Co compound. The OMe substitution appears to make a significant improvement in the measured β value. These compounds are most closely related to simple acceptor substituted aromatic compounds, since the PMK ligand is not substituted. For comparison the β value for nitrobenzene is $2 \times 10^{-30} \text{ esu}$. The metal PMK complexes compare favorably to nitrobenzene. It will be very interesting to see how the other donor substituted PMK complexes compare to their organic counterparts.

Ratner has shown that data from Zerner's INDO/S electronic structure formalism (ZINDO) can be used to calculate β values for organometallic molecules with reasonable accuracy. The version of ZINDO we have access to now is on a Tektronics Cache system. The calculated electronic spectrum is very close to that measured for the cobalt complex. Unfortunately, this version of the program has been adapted to generate electronic spectra, and the routines used to calculate transition dipole moments between different excited states removed. These transition dipole moments are needed to calculate β by a sum-over-states method. With the data generated by ZINDO a simpler two level model can also be used to approximate β . This model assumes that β can be approximated by considering only a single charge transfer transition. From the ZINDO output we can screen for transitions with large

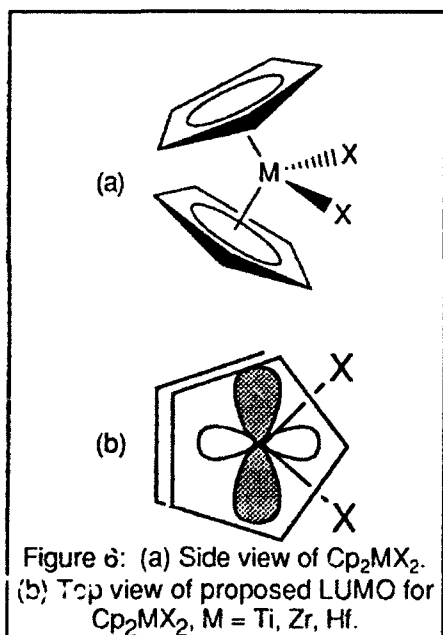
oscillator strengths and $\Delta\mu_{eg}$ values (both needed to give a large β in the two level approximation). The intense lower energy transitions are ligand-ligand transitions with relatively low β s. The low β value here is not too surprising. The types of transition that would be expected to contribute most to β are ligand-to-metal charge transfers (LMCT). The ligand orbitals that are most suited for LMCT are of π symmetry, and all of the π symmetry (t_{2g} set) are filled for Co^{III} . The more interesting molecules to study are those where the t_{2g} set is only partly filled, which have larger experimental β values. The ZINDO calculations for the Sc, Cr and Fe compounds show LMCT bands in the electronic spectra, but also give relatively low β values. We have recently become involved in a collaboration with Ratner's group and plan to calculate the β values for these complexes at Northwestern.

3rd Order NLO Properties of Organometallic Complexes

A recent report of good NLO properties found for groups 10 metal acetylide oligomers suggests that organometallic complexes may be good candidates for NLO study. Electron delocalization in these electron-rich organometallic complexes is achieved by strong metal to ligand charge transfers between the filled metal orbitals and vacant acetylide π^* orbitals. Early transition metal complexes, in contrast to the late transition metals, are often electron poor. Group 4 metallocene complexes, Cp_2MX_2 , $\text{M} = \text{Ti, Zr, Hf}$, are formally d^0 , 16 electron complexes. Theoretical calculations show that the LUMO in these complexes is primarily a metal centered orbital, which lies in the MX_2 plane, as shown in Figure 6. Strong π donation and ligand to metal charge transfer (LMCT) involving this vacant metal orbital are observed for amide and alkoxide ligands; spectroscopic evidence suggests LMCT processes may be important in acetylide complexes as well. This LMCT interaction may lead to mixing between the π systems of the acetylide ligands to produce an extended network. We have examined the third order NLO properties of group 4 metallocene acetylide complexes.

Group IV metallocene complexes were purchased or synthesized using literature procedures. The third order nonlinear optical susceptibilities, γ , were derived from the third harmonic generation (THG) efficiencies found for solutions of a given metal complex (fundamental: 1907 nm, third harmonic: 636 nm). This chemistry is discussed in references 5 and 9.

In order to have a basis for understanding the third order properties of Group IV metallocenes, we first undertook a study of the metallocene halide complexes. The lowest lying absorption in the UV-Vis spectrum of these molecules arises from a Cp to metal charge transfer. This charge transfer could give rise to measurable nonlinear optical properties for these complexes. The third order susceptibilities of these complexes are too low to allow them to be determined exactly, even for saturated solutions (approximately 0.15M). The γ s are $< 5 \times 10^{-36}$ esu. The conclusion from these studies is that the Cp to metal charge transfer does not lead to an extended π system with a measurable γ . For comparison, the γ measured for benzene is 4×10^{-36} esu. Group 8 metallocenes give relatively larger values of γ . 1,1'-dibutylferrocene (BuFc) is a liquid at room temperature. The γ derived from a THG experiment on neat BuFc is 25×10^{-36} esu. Prasad reports a value for normal ferrocene (Cp_2Fe), determined by degenerate four wave mixing, of 16×10^{-36} esu. The difference between the two numbers is most likely due to differences in the measurement techniques and not inherent nonlinearities.



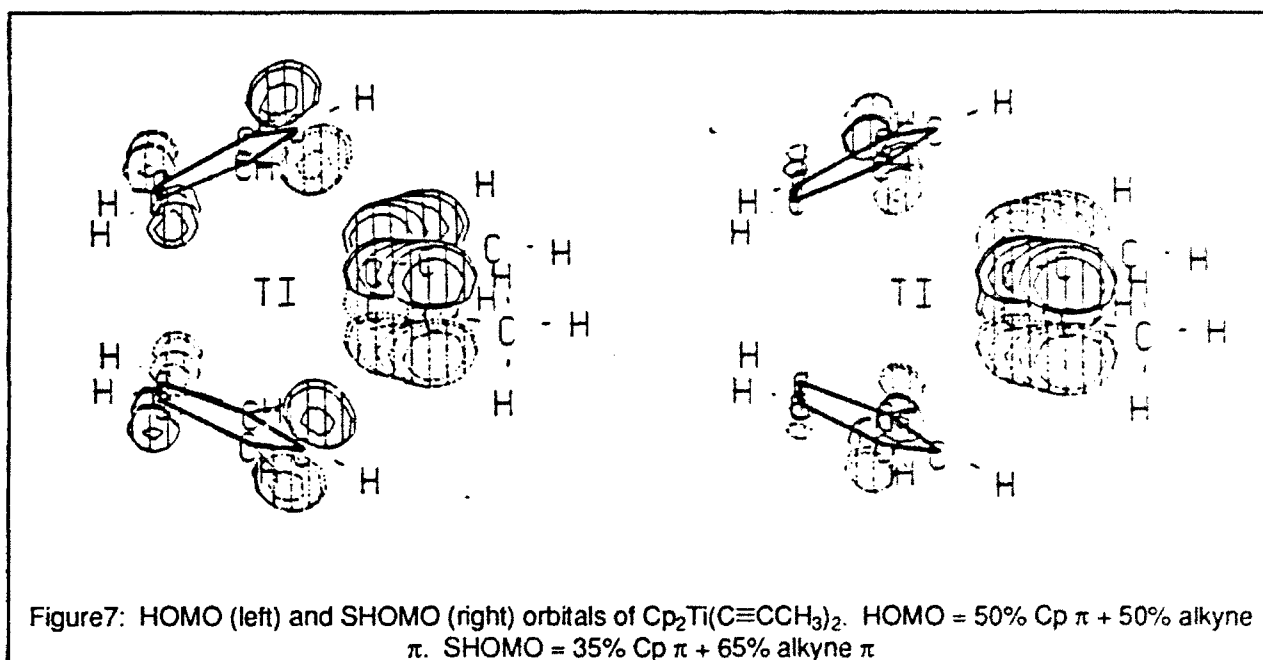
The metallocene phenylacetylide complexes have γ values ranging from 50 to 90×10^{-36} esu, which are good relative to comparable organometallic and organic molecules studied to date. $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CPh})_2$ has a γ value 15 times that of phenylacetylene and twice that of diphenylbutadiyne. There is a definite trend in the metal containing complexes: as one goes down the periodic chart γ decreases. The monosubstituted Ti-acetylide complex gives a γ which is approximately one third of the bis substituted complex.

One possible explanation for the increase in γ of these metal complexes over their organic analogs is that the Cp_2M moiety is acting as an electron accepting group for each phenylacetylene ligand independently, and not linking them. Studies have shown that acceptor substituted organic compounds have increased third order susceptibilities over their unsubstituted analogs. For example β -nitrostyrene has a γ of 29×10^{-36} esu, compared to 17×10^{-36} esu for styrene itself. If the Cp_2M unit is acting as a simple electron accepting group, the γ value for $\text{Cp}_2\text{Ti}(\text{Cl})\text{C}\equiv\text{CPh}$ should be at least half of that observed for $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CPh})_2$. The measured value for the monophenylacetylide is *ca* one third that of the bisphenylacetylide, demonstrating that the metal is not just a simple Lewis acid.

The second possibility is that the acetylide units are effectively linked through a charge transfer process involving the metal and acetylide π orbitals, our original hypothesis for studying these materials. The decreasing trend in γ s ($\text{Ti} > \text{Zr} \geq \text{Hf}$) is rationalized by assuming that the Ti d orbitals are closer in energy to the alkynyl π orbitals than the Zr d orbitals are, which leads to more significant mixing for the Ti complexes as compared to the zirconium or hafnium complexes. This smaller energy gap between the metal and organic ligand orbitals is seen in the absorption spectra (Ti is red shifted relative to Zr or Hf).

A third possibility for the electronic structure leading to the observed NLO properties involves only the Cp and alkynyl ligands. An *ab initio* calculation carried out on $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{Me})_2$ suggests that extensive mixing occurs between the π symmetry Cp orbitals and the alkynyl π orbitals (*vide infra*). These alkynyl π orbitals are orthogonal to the metal centered LUMO. This mixing leads to an extended π system that involves only the organic ligands, and not the metal. The trend in the metals in this case would be explained by the differences in the radii of the metal ions ($\text{Ti} < \text{Zr} \approx \text{Hf}$). Titanium's smaller radius brings the organic ligands closest together, enhancing the orbital overlap and mixing, leading to the largest γ .

Ab initio calculations carried out on $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CH})_2$ suggest that there is extensive mixing between the alkynyl π orbitals and the π symmetry orbitals of the Cp rings. These calculations are discussed in reference 6. Geometries were obtained at the STO-3G level for $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CMe})_2$, using GAUSSIAN '86 on a VAX 30400. Bond lengths and angles in the optimized



structure are consistent with similar titanocene structures. Single point calculations were also carried out at 3-21G, 3-21G* and 6-31G levels on $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CH})_2$. The best description of the top two filled orbitals based on these calculations are mixtures of *ca* 60% Cp and 40% alkynyl π orbitals, figure 7. ZINDO calculations carried out on this molecule show the same mixing in the top two filled orbitals, and predicted large oscillator strength for the transition between the HOMO and a predominantly π^* state (very little metal character) three levels up from the LUMO.

In order to test if this interaction between organic ligands and Cps is important we examined $\text{Cp}_2\text{Zr}(\text{Cl})-\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CH}-\text{Zr}(\text{Cl})\text{Cp}_2$. In this complex the π system of the vinyl ligand is held in an orientation that can not interact with the metal based LUMO, but can interact as shown above. The measured γ for this complex is 150×10^{-36} esu, suggesting that the out of plane interaction is important for forming large delocalized systems in these complexes. Related molecules with "out of plane" π systems were examined and show the same trend in γ values. A range of interesting molecules based on the metallocene framework are being investigated for third order NLO study.

Layered Polymer Composites

The research discussed in this section of the report was not described in the proposal funded by the AFOSR, but represents a new area we have gone into that may lead to some very interesting and novel materials, and is discussed in reference 3. These materials are structurally related to simple intercalation compounds. Intercalation compounds are formed by treating a layered host compound with a suitable guest, as shown in Figure 8. The driving force for this intercalation is typically an acid/base reaction. The intercalated "crystal" is usually highly ordered along the axis perpendicular to the layers, but is poorly ordered along the other two axes. We have found that if the guest molecules are acetylenic or diacetylenic amines, that polyacetylenes and polydiacetylenes can be formed between the host layers by irradiating the intercalation complex with UV light or heating to 170°C. The resulting material has alternating organic polymer and inorganic layers.

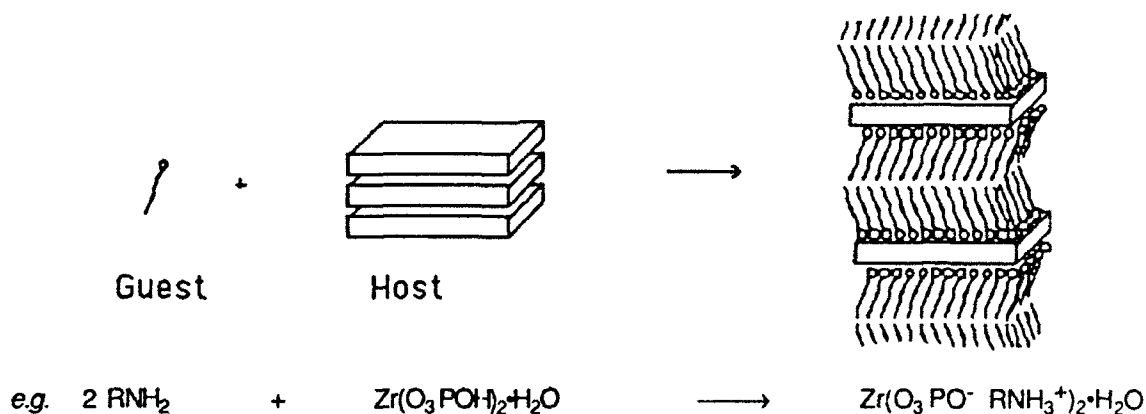


Figure 8: An intercalation reaction.

In most cases intercalation reactions involve microcrystalline host samples (1-50 μM) that react with the guest molecules in a heterogeneous reaction, leading to powdered intercalation compounds. These powdered samples are of little use for optics, since the scattering losses are severe. Fortunately, some hosts intercalate by a different pathway. It has been well documented for clays and metaldichalcogenides that, under the appropriate conditions, the first step can be exfoliation, figure 9. This exfoliated material then reconstitutes into a layered material with the guest incorporated. Using this process it is

possible to get host layer particle sizes to well below a micron, thus decreasing scattering losses significantly.

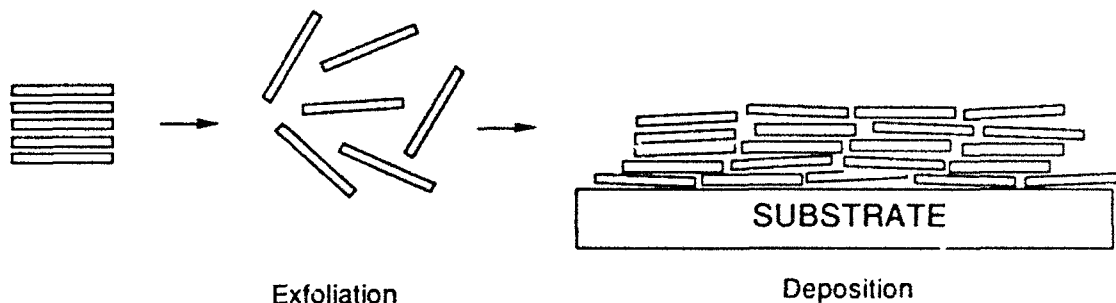


Figure 9: Schematic representation of an exfoliation and reconstitution of a layered material. The guest molecules are not shown. The reconstituted material on the left will have guest molecules completely surrounding the host lamella and crystals.

Propargylamine ($\text{HC}\equiv\text{CCH}_2\text{NH}_2$) reacts with $\text{Zr}(\text{O}_3\text{POH})_2\cdot\text{H}_2\text{O}$ by the conventional means, *i.e.* a heterogeneous reaction. The same amine, however, reacts with $\text{Sn}(\text{O}_3\text{POH})_2\cdot\text{H}_2\text{O}$ by first exfoliating the solid to give a clear orange solution, then on removal of solvent a yellow crystalline film is deposited. The powder x-ray diffraction pattern found for this film is nearly identical to that found for $\text{Zr}(\text{O}_3\text{PO}^- \text{HC}\equiv\text{CCH}_2\text{NH}_3^+)_2\cdot\text{H}_2\text{O}$, which is formed by the typical heterogeneous reaction and has a structure similar to that shown in figure 8. Elemental analysis shows these thin film materials are rich in propargyl amine, relative to simple intercalation compounds. The Sn compound analyzes as $\text{Sn}(\text{O}_3\text{PO}^- \text{HC}\equiv\text{CCH}_2\text{NH}_3^+)_2(\text{HC}\equiv\text{CCH}_2\text{NH}_2)_{0.3}$. The excess propargyl amine presumably fills the the spaces between crystallites in the thin film. The film formed for the Sn compound is patchy; some areas are transparent to the eye and some are opaque. Examination of these films by SEM shows that the opaque areas are made up of large particle sized materials, while the transparent regions are made up of much smaller particle sized materials. Upon heating to 170°C the propargylamine polymerizes and the yellow film turns red. This material is a conjugated polymer with inorganic slabs suspended in it, all of the slabs are parallel and lie parallel to the slide the film is cast on to.

Films can be made transparent by removing the larger particle sized materials, using centrifugation and filtration through millipore filters (0.2 and $0.45 \mu\text{M}$) before preparation of

thin films. A clear thin film was prepared, which was 0.5 μM thick and examined for its wave guiding ability and third order NLO properties in George Stegeman's laboratory at CREOL. Unfortunately, the films gave no measureable THG. We are currently trying to find ways to prepare similar films with other amine substituted guests (*i.e.* diacetylenes) to examine how the NLO properties of these films are effected by structural and electronic changes.

With AFOSR support we have also developed dependabel routes into stable layered inorganic/organic materials, which will be significantly more stable and better ordered than the materials described above. This work is discussed in reference 4.

Papers written on chemistry supported by this grant:

1. Synthesis and Nonlinear Optical Properties of Inorganic Coordination Polymers. William Chiang, Mark E. Thompson, Donna Van Engen, "Organic Materials for Nonlinear Optics", R.A. Hann, D. Bloor (Eds.), Royal Chemical Society, London, 1990, in press.
2. Nonlinear Optical Properties of Inorganic Coordination Polymers and Organometallic Complexes. Mark E. Thompson, William Chiang, Lori K. Myers, Charles Langhoff. *Proc. SPIE*, 1991, 1497, 423-429.
3. Synthesis and Polymerization of Propargylamine and Aminoacetonitrile Intercalation Compounds. John E. Pillion and Mark E. Thompson. *Chemistry of Materials* 1991, 3, 777-779.
4. The Synthesis of Amide and Ester Intercalation Compounds from $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{COCl})_2$. David A. Burwell and Mark E. Thompson, *Chemistry of Materials* 1991, 3, 730-737.
5. Cubic Nonlinear Optical Properties of Group 4 Metallocene Halide and Acetylide Complexes. Lori K. Myers, Mark E. Thompson and Charles Langhoff, *J. Am. Chem. Soc.*, 1992, 114, 7560-7561.
6. Structure and Bonding in Group 4 Metallocene Acetylide and Olefin Complexes. Eugene T. Knight, Lori K. Myers and Mark E. Thompson, *Organometallics*, 1992, 11, 3691-3696.
7. The Synthesis and Structures of Polar Coordination Polymers; $[(\text{SALEN})\text{MnO}_2\text{CCH}_2\text{D-B}]_n$, D = NH, S; -B: = 4-pyridyl, 4-benzonitrile. William Chiang, Mark E. Thompson, Donna Van Engen and Douglas Ho, *Inorg. Chem.*, in press.
8. Second Order Nonlinear Optical Properties of Picolymethylketone Coordination Complexes in Poled Polymer Thin Films. Dennis McCarty, Ajai Nahata, Mark E. Thompson, manuscript in preparation.
9. Cubic Nonlinear Optical Properties of Group 4 Acetylide and Vinyl Complexes. Lori K. Myers, Mark E. Thompson and Charles Langhoff, manuscript in preparation.
10. Chiral Coordination Polymers. William Chiang, Mark E. Thompson, and Douglas Ho, manuscript in preparation.

11. Second Order Nonlinear Optical Properties of (SALEN)Fe(py)X, X = N₃, SCN, F, Cl, Br, I. William Chiang, Mark E. Thompson, Donna Van Engen, manuscript in preparation.